



# Aramid fiber with excellent interfacial properties suitable for resin composite in a wide polarity range

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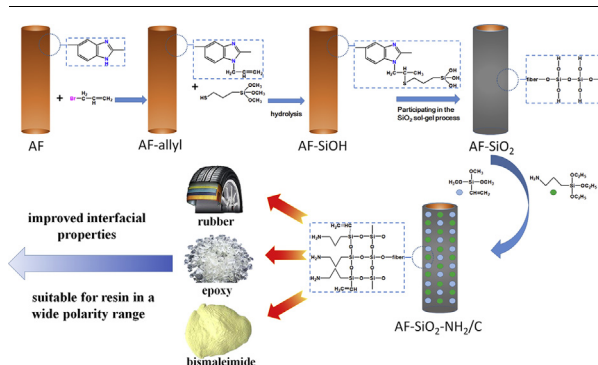
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## HIGHLIGHTS

- Aramid fiber was decorated with SiO<sub>2</sub> structure and high density of NH<sub>2</sub> and C=C groups.
- The modified fiber exhibits excellent interfacial properties with different resins.
- The modification method is confirmed as nondestructive to fiber's tensile strength.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

The weak interfacial adhesion of aramid fiber with resin matrix is believed as a major limitation for its wide application. In this study, a nondestructive grafting method was applied for surface modification of benzimidazole-contained aramid fiber. Using the NH in benzimidazole unit as active sites, aramid fiber surface was firstly decorated with densely SiO<sub>2</sub> structure, and a rough surface was obtained. Then, high density of NH<sub>2</sub> and C=C groups were introduced on fiber surface by the reaction with silane coupling agents. These functionalized NH<sub>2</sub>/C=C groups endow the fiber with the ability to chemically bonding with resin in a wide polarity range, including rubber, bismaleimide and epoxy resin. Also, the SiO<sub>2</sub>-decorated rough surface improves the level of mechanical interlocking with them. Experimental results show that the interfacial shear strength of functionalized fiber with natural rubber, bismaleimide and epoxy resin correspondingly increases 117%, 166% and 43%, compared with that of untreated fibers. Meanwhile, the grafting method is confirmed as nondestructive, and the superior mechanical property of aramid fiber is preserved. In all, the study presents a new effective method for the preparation of aramid fiber with excellent interfacial properties suitable for resin composite in a wide polarity range.

## 1. Introduction

Owing to its superior mechanical properties, especially high strength-to-weight ratio, low density and heat resistance, aramid fiber has been utilized as ideal reinforcement for polymer-based composites,

which is called aramid fiber reinforced polymer composites (AFRP) [1,2]. It has been widely used in various civilian and military fields, including aramid/rubber for tire cord and automobile rubber hose [3], aramid/epoxy and aramid/bismaleimide for airplane structure material [4], aramid/polypropylene for sports equipment. However, a crucial

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problem it faces for application is the poor adhesion between fiber/matrix interface, which is resulted from fiber's inert surface [5]. As is known to all, the adhesion of composite interface plays an important role in composite by transferring the stress from matrix to fiber. So, AFRP usually doesn't show the performance as expected.

Commonly, the adhesion of fiber/polymer interface is strongly determined by three kinds of interactions. They are (1) mechanical interlocking [6,7]; (2) polarity matching [8]; (3) chemical bonding [9,10], and those interactions could be correspondingly promoted by introducing large surface area, van de vales force/electrostatic interaction and chemical bonds between fiber and resin. Numerous efforts have been reported for fiber's surface modification to import these interactions, including acid-alkali treatment [11], chemical oxidation [12], plasma and gamma irradiation [13], and direct fluorination [14,15]. However, most of those reported methods could only suit for one resin matrix. This is due to the different requirement for the adhesion with different resin matrix, especially for polarity matching. Since those resins enhanced by aramid fiber in different fields are in a wide polarity range, they require fiber in different polarity for polarity matching. For example, to improve the adhesion of fiber/epoxy matrix, phosphoric acid was applied for the generation of the  $-COOH$  and  $-OH$  groups on fiber surface [16,17], and the surface polarity is improved. As a result, the composite interfacial adhesion is increased by the increased electrostatic interaction and van der vales forces between fiber and epoxy. When it is applied for natural rubber matrix, the aforementioned method is not suitable, because rubber matrix requires a low polarity of aramid fiber surface, and the introduction of  $-COOH$  and  $-OH$  could even deteriorate the van der vales force in the interface. So it is a big challenge to propose a universal method for the improvement of interfacial adhesion of aramid fiber with resin matrix in a wide polarity range.

Since different polymer matrix system demands different level of polarity for polarity matching, improving one may negatively impact another. Therefore, mechanical interlocking and chemical bonding are considered to be introduced at the interface for the improving the composite adhesion [18], which could universally benefit the adhesion with all kinds of resins.

Considering all these surface modification techniques, chemical grafting seems to gain most traction to achieve the goal for highly mechanical interlocking and chemical bonding [19]. Basing on various reactions, it could cost-effectively make substrates meet the requirement for application. Therefore, various functional groups could be grafted and rough surface could be designed for aramid fiber to obtain a highly functionalized surface, and it would be suitable for matrix in a wide polarity range.

PBIA (Poly-p-phenylene-benzimidazole-terephthalamide) fiber (chemical structure shown in Fig. 1) [20], is a kind of benzimidazole-contained aramid fiber. It is modified from poly (p-phenyleneterephthalamide) (PPTA) fiber by the introducing of 2-(4-Aminophenyl)-1H-benzimidazole-5-amine (PABZ) as the third monomer by co-poly-condensation, and the ratio of PABZ to p-phenylenediamine in the copolymer is 1:1. Owing to the introduction of PABZ, PBIA has a superior mechanical strength and higher interfacial properties. Meanwhile, the introduced benzimidazole group endows the fiber with active sites for functionalization.

In this study, aramid fiber with excellent interfacial properties was prepared by surface designing, and it suits for resin matrix in a wide polarity range. Compared with untreated fiber, the modified fiber

possesses higher interfacial adhesion with various matrix, including epoxy, natural rubber and bismaleimide. The whole process is illustrated in Fig. 2. First, through the reaction between the benzimidazole NH and bromopropylene, allyl group was grafted as pendent groups on fiber's macromolecular chain. Second, by further grafting and hydrolysis, Si-OH group was generated by the reaction between trimethoxysilylpropanethiol and fiber's allyl group. Third, by participating in the  $SiO_2$  sol-gel process, the Si-OH group acted as seeds for the generating of  $SiO_2$  layer on fiber surface, and a rougher surface was obtained. Meanwhile, the quantity of Si-OH group gets a great increase by the deficient condensation reaction of  $SiO_2$  in sol-gel process. Last, by the condensation reaction with 3-aminopropyltriethoxysilane and vinyltrimethoxysilane, those numerous Si-OH groups on  $SiO_2$  were used as active sites for the final functionalization of  $NH_2$  and  $C=C$  groups. Therefore, the obtained fiber surface was decorated by both rough  $SiO_2$  structure and high density of  $NH_2$  and  $C=C$  groups, which correspondingly increase the level of mechanical interlocking and import chemical bonding with various resins, and finally it realizes the improvement of interfacial adhesion with polymer matrix in a wide polarity range.

## 2. Experiments

### 2.1. Materials

Benzimidazole-contained aramid fiber was purchased from Chengrand Research Institute of Chemical Industry Co., Ltd. Before using, benzimidazole-contained aramid fiber was washed by soxhlet extractor at  $100^\circ C$  for 12 h, ethanol as solvent. Then it was dried in vacuum oven, and the obtained fiber was denoted as AF in this study. Bromopropylene, trimethoxysilylpropanethiol (TMSP) and vinyltrimethoxysilane (VTMOS) were obtained from Aladdin Co. Ltd. Other chemicals, including NaOH, tetrabutylammonium bromid, hydrochloric acid, tetraethyl orthosilicate (TEOS), azodiisobutyronitrile (AIBN) and 3-aminopropyltriethoxysilane (APTES) were brought from Kelong Chemicals Co. Ltd. All these chemical reagents were used as received.

### 2.2. Surface modification of aramid fiber

#### 2.2.1. Grafting allyl as pendant group on fiber surface

First, 1 g Aramid fiber was put in a 100 ml flask, then 30 mmol bromopropylene and 80 ml dimethylacetamide were added in the flask, and the solution was magnetic stirred at  $25^\circ C$  for 48 h. The grafting reaction was catalyzed by NaOH, and tetrabutylammonium bromid was used as co-catalyst. After the reaction, the fiber was washed by soxhlet extractor to eliminate the residual bromopropylene. The obtained fiber was denoted as AF-allyl.

#### 2.2.2. Grating Si-OH as pendant group on fiber surface

1 g AF-allyl was immersed in 80 ml dimethylacetamide in a 100 ml flask, and 30 mmol TMSP and 1 mmol azodiisobutyronitrile were further added in. The reaction was placed in oil bath and maintained at  $60^\circ C$  for 2 h. After that, the fiber was taken out and washed by soxhlet extractor for 12 h, using ethanol as solvent. Further, the siloxane group of TMSP was hydrolyzed by putting the TMSP-modified AF-allyl into dilute hydrochloric acid (PH = 5) for 1 h at room temperature to generate Si-OH group. The obtained fiber was denoted as AF-SiOH.

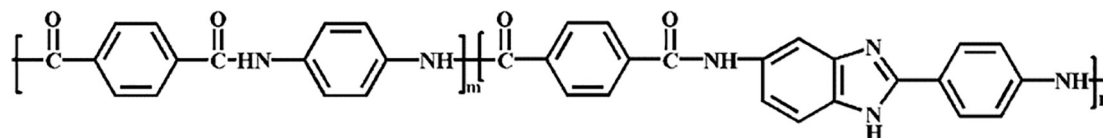


Fig. 1. Chemical structure of PBIA fiber.

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